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Effect of deposition conditions on thickness and permeability of the multilayer films formed from natural polyelectrolytes

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ABSTRACT

Formation of films from natural polyelectrolytes opens a wide range of application in the areas like tissue engineering, implantation of medical devices or other medical fields. The permeability of films, fabricated from the natural polyelectrolytes by using the layer by layer method, was determined by the cyclic voltamperometry. Using the electroactive molecules that differ in molecular size the porosity of films was examined. We compared the thickness and permeability of multilayer films composed from biocompatible and natural polyelectrolytes with ones composed from the model polycation/polyanion pair, PAH/PSS (polyallylamine hydrochloride/poly(4-styrenesulfonate)). We attributed the difference in the permeability of films with similar thickness to the higher chain stiffness of natural polyelectrolytes. The effect of the anchoring PEI (poly(ethyleneimine)) layer was also examined.

1. Introduction

One of the most promising techniques of surface modification by polyelectrolytes was presented by Decher et al. in the beginning of the 1990s [1]. It is called the sequential adsorption or "Layer by layer" deposition. This technique possesses several advantages. First of all it is very simple: the substrate is exposed sequentially to aqueous solutions of oppositely charged polyelectrolytes. A wide variety of water-soluble polyions or nanoparticles can be used as components: linear or branched polyelectrolytes, proteins, viruses, dendrimers, metallic, oxide, clays or silica particles, quantum dots, etc. Polyelectrolyte multilayers can be formed in many geometries; the most important are: PEMs adsorbed on planar interfaces as coatings, adsorbed on particles or as detached membranes for filtration and also as membranes for encapsulation of solid or liquid cores [2–4]. Another reason for the popularity of the LbL method is it's the ability to create highly tailored polymer thin films with unlimited range of functional groups or nanoobjects incorporated within the film structure. Since most biopolymers (like DNA) are charged, polyelectrolytes play an important role in the field of biomolecules. Many of the biological processes require understanding of the interaction between biopolymers and objects of colloidal size such as proteins or cells [5]. The use of the biopolymers to create multilayer film carries great potential for application in the areas such as tissue engineering, implantation of medical devices and artificial organs, prostheses, ophthalmology, dentistry, bone repair and many other medical fields [6–8]. Polymer based delivery systems enable controlled release of drugs into the body. They also make possible targeting of drugs into sites of inflammation or tumors. For such purpose, prodrugs, are also used. The term prodrugs describe a harmless molecule, which undergoes a reaction inside the body to release the active drug. They are obtained by conjugating of biocompatible polymeric molecules with appropriate drugs. The prodrugs accumulate in tumors because the permeability of cell membranes of tumor cells is higher than that of normal cells [6]. The controlled release technologies are becoming more and more important, especially in release of tailored drugs. They have a large advantages over traditional forms of drug dosage in a number of ways, for example: minimizing deleterious side effects, prolonging time of activity and protecting sensitive drugs from enzymatic or acidic degradation in the gastrointestinal track [9,10]. Use of polyelectrolyte films as capsules shells allows regulation of the release rate of the enclosed active agents [11,12]. Moreover, that type of shell can be easily functionalized to reduce toxicity, decrease interaction of capsules with the immune system ("stealth effect") [13] and by immobilization of target specific ligands, used for the intelligent delivery systems.

To fabricate nanoporous multilayered films of desired properties, different pH, temperature or ionic strength of their solutions can be used. By the brakeage of the interchain ionic bonds and rearrangement of the polyelectrolytes inside the film, it is possible to obtain polyelectrolyte films of different structures. For example, Rubner et al. prepared nanoporous thin film from the PAH/PSS polyelectrolyte by changing the external pH [14,15].

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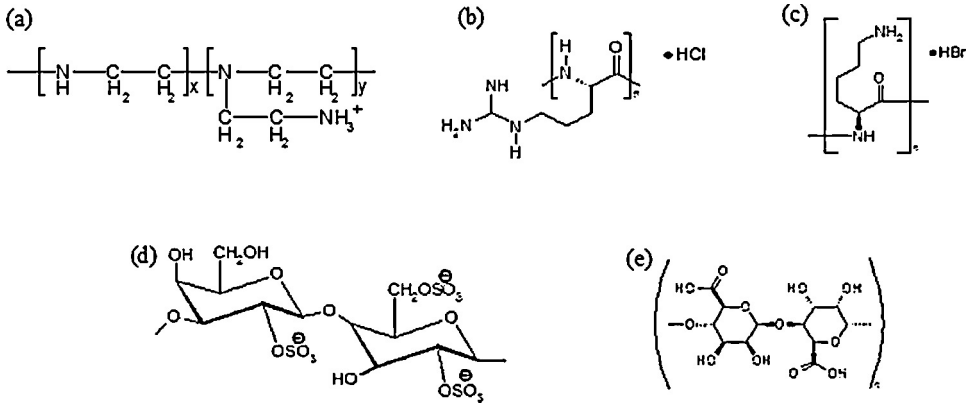

Fig. 1. Structural formulas of used polyions: (a) poly(ethyleneimine), (b) poly(L-arginine hydrochloride), (c) poly(L-lysine hydrobromide), (d) λ-Carrageenan, (e) alginic acid sodium salt.

As stated above, the permeability of polyelectrolyte membranes plays a key role in many potential applications, especially in the context of the controlled release the substance (like drug, dye) from inside of the capsules. Chitosan and alginate have been mostly used to prolong the permeation of target compounds [16–18]. Such systems have extremely high potential in the pharmaceutical area to encapsulate real drugs rather than model molecules [19–22]. The optimal drug release requires the drug not only to be released with controlled rate but also transported to the target site with less loss [23]. Application of natural polyelectrolytes membranes is very important in medical sciences [24–27] since they are non-toxic and can undergo decomposition in patient bodies without causing side effects. The biocompatible films bring great potential, focusing on medical issues, such as promotion of cellular adhesion, microcapsule coatings, drug delivery. Therefore, a deeper understanding of mechanisms controlling their permeability, which is the subject of this paper, is a very important step in completing the knowledge about characteristics of the polyelectrolyte multilayer films deposited on macroscopic surfaces and colloidal particles.

In our recent work [28], we demonstrated that the cyclic voltamperometry (CV) technique using electroactive probes which differ in the molecular size could be the useful method to determine the permeability of multilayer membranes formed from model, synthetic polyelectrolytes. Because of their biomedical importance, in this paper, our attention was focused on formation of multilayer films from natural polyelectrolytes. We compare thickness and permeability of model PAH/PSS multilayer films with ones formed from selected pair of biocompatible and natural PE, poly(L-arginine)/λ-Carrageenan. For the latter purpose three electroactive probe molecules of different molecular size were selected for that purpose: *p*-benzoquinone (pBQ), 1,2-naphthoquinone-4-sulfonic acid sodium salt (NQS) and manganese(III) 5,10,15,20-tetra(4-pyridyl)-21*H*,23*H*-porphine chloride tetrakis(methochloride) (MnP). We examined: effect of the ionic strength of polyelectrolyte solution and first anchoring layer of branched poly(ethyleneimine).

2. Materials and methods

2.1. Materials

We used the following polyelectrolytes to form multilayer films at the surface of Si/SiO_2 wafers (ellipsometry) and gold electrode (CV). Polycations: branched poly(ethyleneimine) (PEI) (MW ~ 70 kDa), poly(L-arginine hydrochloride) (Arg) with molecular mass 15–70 kDa, poly(L-lysine hydrobromide) (PLL) (30–70 kDa). Polyanions: λ-Carrageenan (Car) and alginic acid sodium salt (Alg). Poly(L-arginine hydrochloride), PLL, λ-Carrageenan and alginic acid sodium salt were purchased from Aldrich, while PEI was obtained from Polysciences, USA. The structures of polyions used in our studies are presented in Fig. 1.

Silicon wafers were purchased from On Semiconductor, Czech Republic. Before experiments silicon wafers were cleaned with piranha solution and rinsed with hot, distilled water (70 °C). Adsorption of polyelectrolytes was performed by layer-by-layer method from NaCl (99.5% Fluka) solutions of constant ionic strength (0.015 M, 0.15 M and 0.75 M, respectively), with the concentration of PE 0.1 g/L. It was high enough to establish a saturated adsorbed layer during the 10 min adsorption step. Si/SiO_2 substrates were first immersed in polycation and then rinsed three times for 2 min with distilled water. Then the sample with a monolayer adsorbed was dipped in polyanion solution and rinsed. The procedure was repeated until the required number of layers was obtained. After formation of the film the wafers were carefully dried in a stream of nitrogen at the room temperature to remove the water film from the surface and to avoid contamination with the dust. For voltamperometric studies the multilayer was formed at the surface of the gold electrode using the same LbL procedure. The electroactive redox probes: pBQ, NQS and MnP were obtained from Aldrich. The concentration of electroactive molecules in CV experiments was 10^{-3} g/L.

3. Methods

3.1. Ellipsometry

Optical parameters of dried polyelectrolyte films: refractive index, absorption coefficient and their thickness were determined using EP^3 single-wavelength multiangle imaging ellipsometer (Nanofilm). Measurements were carried out in autonulling mode in PCSA configuration (polarizer-compensator-sample-analyzer). To obtain the film thickness in the single wavelength ellipsometric experiment, it is necessary to determine its optical constants: refractive index (n) and extinction coefficient (k). These parameters can be established by using multiple angle of incidence analysis [29]. The optical constants were calculated by fitting elliptical parameters obtained during the measurements to the appropriate model (Si/SiO_2/PE film/air). The determined value of refractive index was equal to 1.55, while the absorption coefficient was negligibly small. The ellipsometric thickness of multilayers was measured at the 75° angle of the incidence, near the Brewster angle for the support material (silicon-SiO_2 wafer) [30] in order to obtain results with the highest possible sensitivity.